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Homogeneous Supported Synthesis Using Ionic Liquid Supports: Tunable Separation Properties

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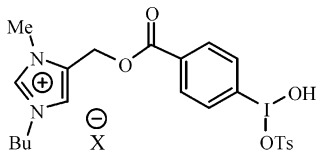
Received December 15, 2004



X = NTf_2 or OTs

We report a homogeneous supported version of Koser's salt based on a room-temperature ionic liquid (RTIL) support. By altering the nature of the RTIL, a material was developed that was stable, recyclable, and readily separable from the tosyloxylated ketone products just by using variations in solvent polarity. A similar approach should be applicable to a wide range of supported catalysts and reagents.

Room-temperature ionic liquids (RTILs) are not only gaining greater attention as solvents for organic synthesis but also increasingly finding applications in other areas as well.[1] One of the more recent developments is the use of RTILs as homogeneous supports. Much of this interest has been in the area of homogeneous supported synthesis.[2,3] Bazureau and co-workers have been the most active in this area and used ester linkages to tether various small molecules to an ionic liquid core and then employed condensation reactions to create compounds such as thioxotetrahydropyrimidinones and thiazolidinones.[2] Other workers, including ourselves, have similarly used ester linkages for the support of small molecules such as acrylates and iodobenzoates, which have then be employed in further transformations.[3−5] Only in one case has a different linkage been used. In this case, an amine linkage was formed and the final product released by hydrogenolysis, resulting in a RTIL support that could not be recycled, unlike the ester linkage supports.[6]

At the same time, far less effort has been spent on RTIL-supported reagents. RTILs themselves have been supported on silica or have been used as recyclable reagents, but the idea of supporting a reagent on a RTIL is far less studied. Most existing reports focus on the support of metal catalysts, such as vanadyl salen complexes[7] and ruthenium metathesis catalysts.[8] These species were not only catalytically active, but were also readily retained in RTIL layers and thereby recycled. In terms of nonmetallic reagents, the only existing reports all deal with either sulfonic acids[9] or sulfonyl chlorides[10] supported on RTILs, the former of which are recyclable acid catalysts, while the later are consumed reagents for Friedel−Crafts alkylations or Beckman rearrangements.

Our particular interest was in the preparation of supported stoichiometric reagents, not catalysts. In particular, we viewed hypervalent iodine reagents such as diacetoxyphenyliodane and Koser's salt as appealing challenges to the RTIL supported method.[11] The reasoning behind this selection is 2-fold. First, reactions involving any of these reagents ultimately involve the separation of the iodobenzene byproduct from the desired product. Although this can be accomplished via chromatography, it does necessitate a chromatographic separation step and precludes the direct use of the reaction products in subsequent reactions. This is particularly an issue in cases where the reaction products are sensitive and decompose on silica gel (vide infra). Second, these hypervalent iodine reagents are generated from iodobenzene. Although this same material can, in theory, be recovered at the end of the reaction, in practice it rarely is due to the extra effort required for recovery, purification, and regeneration.

To address the issues associated with iodobenzene recycling, various supported iodanes have been reported, most typically using polystyrene as the support.[12] These supported reagents have been successfully applied in a number of cases and can be recycled. At the same time,

(1) Welton, T. *Chem. Rev.* **1999**, *99*, 2071−2083. Freemantle, M. *Chem. Eng. News* **2000**, 37−50. Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772−3789. Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667−3692. *Ionic Liquids in Synthesis*; Wasserscheid, P., Welton, T., Eds.; Wiley-VCH: Weinheim, 2003.

(2) Hakkou, H.; Eynde, J. J. V.; Hamelin, J.; Bazureau, J. P. *Tetrahedron* **2004**, *60*, 3745−3753. Hakkou, H.; Vanden Eynde, J. J.; Hamelin, J.; Bazureau, J. P. *Synthesis* **2004**, 1793−1798. Fraga-Dubreuil, J.; Bazureau, J. P. *Tetrahedron* **2003**, *59*, 6121−6130. Fraga-Dubreuil, J.; Bazureau, J. P. *Tetrahedron Lett.* **2001**, *42*, 6097−6100.

(3) Handy, S. T. Okello, M. *Tetrahedron Lett.* **2003**, *44*, 8399−8402.

(4) Anjaiah, S.; Chandrasekhar, S.; Gree, R. *Tetrahedron Lett.* **2004**, *45*, 569−571.

(5) de Kort, M.; Tuin, A. W.; Kuiper, S.; Overkleeft, H. S.; van der Marel, G. A.; Buijsman, R. C. *Tetrahedron Lett.* **2004**, *45*, 2171−2175.

(6) Miao, W.; Chan, T. H. *Org. Lett.* **2003**, *5*, 5003−5005.

(7) Baleizao, C.; Gigante, B.; Garcia, H.; Corma, A. *Tetrahedron Lett.* **2003**, *44*, 6813−6816.

(8) Audic, N.; Clavier, H.; Mauduit, M.; Guillemin, J.-C. *J. Am. Chem. Soc.* **2003**, *125*, 9248−9249. Geldbach, T. J.; Dyson, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 8114−8115.

(9) Cole, A. C.; Jensen, J. L.; Ntai, I.; Trans, K. L. T.; Weaver, K. J.; Forbes, D. C.; Davis, Jr.; J. H. *J. Am. Chem. Soc.* **2002**, *124*, 5962−5963. Gu, Y.; Shi, F.; Deng, Y. *Catal. Commun.* **2003**, *4*, 597−601.

(10) Qiao, K.; Yokoyama, C. *Chem. Lett.* **2004**, *33*, 472−473. Gui, J.; Deng, Y.; Hu, Z.; Sun, Z. *Tetrahedron Lett.* **2004**, *45*, 2681−2683.

(11) For recent reviews of hypervalent iodine chemistry, see: Hypervalent Iodine Chemistry: Modern Developments in Organic Synthesis. *Topics in Curr. Chem. Vol. 224*; Springer-Verlag: Berlin, 2003. Koser, G. F. *Aldrichimica Acta* **2001**, *34*, 89−102. Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, *102*, 2523−2584. Varvolis, A. *The Organic Chemistry of Polycoordinated Iodine*; VCH Publishers: New York, 1992.

(12) For examples, see: Chen, J. M.; Lin, X. J.; Huang, X. A. *J. Chem. Res., Synop.* **2004**, 43−44. Lee, J. W.; Ko, K. Y. *Bull. Korean Chem. Soc.* **2004**, *25*, 19−20. Togo, H.; Sakuratani, K. *Synlett* **2002**, 1966−1975. Ficht, S.; Mulbaier, M.; Giannis, A. *Tetrahedron* **2001**, *57*, 4863−4866. Tohma, H.; Morioka, H.; Takizawa, S.; Arisawa, M.; Kita, Y. *Tetrahedron* **2001**, *57*, 345−352. Ley, S. V.; Thomas, A. W.; Finch, H. *J. Chem. Soc., Perkin Trans. 1* **1999**, 669−671.

10.1021/jo047807k CCC: $30.25
Published on Web 03/03/2005

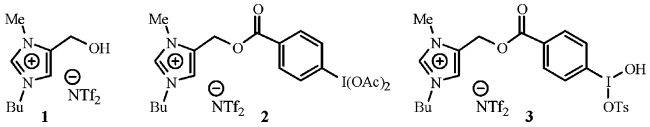
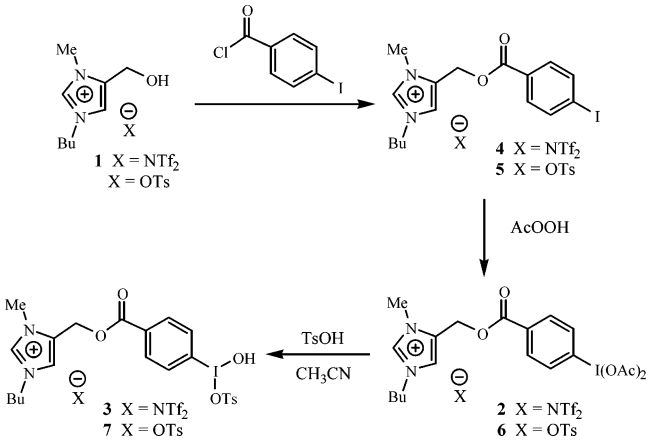


FIGURE 1. RTIL-supported hypervalent iodine reagents.

SCHEME 1. Preparation of Supported Koser's Salt 3



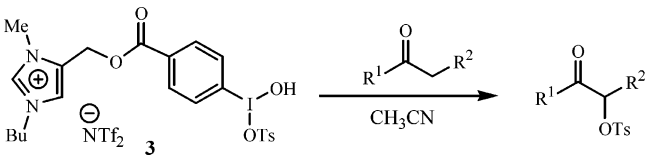
they do suffer from the typical phase transfer problems that plague all hetereogeneous supports, thereby slowing the progress of these reactions. Further, the long-term stability of polystyrene to these oxidizing agents is a concern as well.

Our alternative entry into supported iodane reagents is based upon our previously reported fructose-derived ionic liquid **1** (Figure 1).[13] By attaching commercially available *p*-iodobenzoic acid to this support, a family of iodanes such as diacetoxy compound **2** and Koser's salt **3** can be prepared.

In the event, salt **1** was acylated with *p*-iodobenzoyl chloride to afford supported iodobenzene **4** in nearly quantitative yield (Scheme 1). Oxidation of this compound with peracetic acid under conditions similar to those reported for the preparation of diacetoxyiodobenzene resulted in the preparation of diacetoxy compound **2**.[14] After the removal of all volatiles, the crude residue was used directly to prepare supported Koser's salt **3** by treatment with tosic acid in acetonitrile, again paralleling the procedure used for the parent, nonsupported compound.[15] Following removal of the volatiles, the resulting viscous liquid was used as is in subsequent reactions. ^{1}H NMR indicated the absence of any of iodo compounds **4** or **2**.

With the supported Koser's salt in hand, the α-tosyloxyation of ketones was studied (Table 1). Much to our delight, reagent **3** was effective for this transformation. The α-tosyloxyketones were obtained in >60% isolated yield. Further, the reactions themselves were faster than those with Koser's salt itself, likely due to the presence of the electron-withdrawing ester group on the benzene ring. The only problem was in the separation of supported

TABLE 1. Tosyloxyketone Preparation with Koser's Salt 3



R^1	R^2	conditions	time	% yield[a]
CH_3	H	55°C,))))	20 min	67
Et	CH_3	RT	20 min	80
Ph	H	55°C,))))	20 min	74
$-(CH_2)_4-$		0°C	2 h	65 (76)[b]

[a] Isolated yield. [b] Overnight reaction.

iodobenzene **4** from the reaction products. This salt proved to be soluble in the same range of solvents as the tosyloxyketone products (ether, ethyl acetate, acetone, methylene chloride). Ultimately, the only effective method for separating the products from iodobenzene **4** proved to be chromatography. A quick separation using ethyl acetate/hexanes to elute the tosyloxyketone, followed by acetonitrile to elute salt **4** was reasonably effective and did result in 76−80% recovery of salt **4**. Still, the need to use chromatography negated much of the potential advantage of this supported reagent and the recovery of **4** was far from satisfactory.

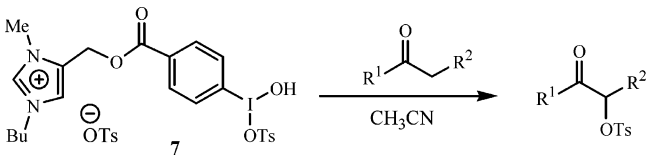
At this point, we turned to one of the advantages of RTIL materials—tunable physical properties. By varying the anion and cation, RTILs can be prepared that vary in polarity, viscosity, density, melting point, and miscibility/solubility properties.[1] In particular, it is known that for imidazolium cation based RTILs, harder anions such as phosphate, tosylate, and chloride generally result in RTILs that are miscible with polar solvents (water, methanol) but not with less polar solvents (ether, ethyl acetate, toluene). On the other hand, softer, more weakly coordinating anions such as hexafluorophosphate and triflimide result in RTILs that are immiscible with polar solvents but miscible with less polar solvents including toluene and ether. With this in mind, it appeared that supported iodane reagents with a more coordinating anion should be a method for obviating the product/byproduct separation issue.

To that end, supported iodobenzene **5**, which has a toluenesulfonate anion, was prepared (Scheme 1). Oxidation with peracetic acid, followed by treatment with tosic acid in acetonitrile then afforded supported Koser's salt **7** as before. During this sequence, it was noted that all of the tosylate salts are more viscous than the triflimide salts. Further, salt **5** is actually a solid at room temperature.

With this second-generation supported Koser's salt in hand, the α-tosyloxyation of ketones was again examined (Table 2). The reactions proceeded slightly slower than with the triflimide salt version of the supported Koser's salt, but were still generally complete within 30 min. The yields were comparable to those obtained before. The real advantage came in the separation phase. With tosylate salt **7**, the byproduct was iodobenzene **5**, which could be readily separated by dilution of the reaction with ether. This reduction in polarity was sufficient to precipitate salt **5**, which could then be recovered in >95% yield by

(13) Handy, S. T.; Okello, M.; Dickenson, G. *Org. Lett.* **2003**, *5*, 2513−2515.
(14) Ficht, S.; Mulbaier, M.; Giannis, A. *Tetrahedron* **2001**, *57*, 4863−4866.
(15) Koser, G. F.; Relenyi, A. G.; Kalo, A. N.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1982**, *46*, 2487−2489.

TABLE 2. Tosyloxyketone Preparation with Koser's Salt 7



R^1	R^2	conditions	time	% yield[a]
CH_3	H	55°C,))))	30 min	60
Et	CH_3	55°C,))))	30 min	57
Ph	H	55°C,))))	30 min	74
$-(CH_2)_4-$		0°C	6 h	79
$-(CH_2)_3-$		55°C,))))	30 min	74

[a] Isolated yield.

simple filtration. The tosyloxyketone product could be isolated following an aqueous workup on the organic layer. In most cases this afforded the pure product, but in some cases a trace of unreacted ketone was observed, which could be readily removed by trituration with cold hexane.

Importantly, the recovered iodobenzene **5** could be converted once again into the supported Koser's salt **7** as before. This material was again capable of carrying out the tosyloxyation reaction and afforded results indistinguishable from the initially prepared material. This recovery/reoxidation sequence could be carried out again and again, with no detectable degradation of the support.

In conclusion, we have reported the application of a RTIL support for recyclable hypervalent iodine reagents. The ability to tune the solubility/miscibility properties of the support by changing the anion greatly facilitates its recovery and demonstrates another method whereby RTIL supports exhibit potential advantages over other supports. Further studies and applications of this concept are underway and will be reported in due course.

Experimental

3-Butyl-4(5)-(4-iodobenzoyloxymethyl)-1-methyl-3*H*-imidazol-1-ium triflimide (4). To a vial containing 0.2590 g of dried ionic liquid **1** (0.5589 mmol) was added 671 μL of dichloromethane followed by 117 μL (0.8383 mmol) of triethylamine. The resultant mixture was cooled to −20 °C, followed by the dropwise addition of a solution of 45 μL (0.5589 mmol) of 4-iodobenzoyl chloride in 112 μL of dichloromethane. The reaction mixture was left to stir for 30 min and then was quenched using 5 N NaOH (200 μL) followed by dilution with dichloromethane (5 mL) and water (2 mL). The aqueous layer was extracted with dichloromethane (3 × 5 mL). The combined organic extracts were dried (Na_2CO_3) and concentrated in vacuo to afford 0.2892 g (quantitative) of **4** as a orange reddish viscous thick liquid which crystallized on standing (mp 71−75 °C): IR ($CHCl_3$) ν_{max} cm^{-1} 3139.2, 3023.0, 2877.4, 1791.7, 1729.9, 1585.6, 1521.1, 1476.7, 1423.2, 1394.8, 1350.0, 1262.0, 1203.5, 1134.0, 1091.4, 1057.7, 1008.9, 996.4, 928.8, 909.7, 848.7, 787.4, 666.8, 625.8; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 8.71 (s, 1H), 7.79 (d, J = 11 Hz, 2H), 7.68 (d, J = 11 Hz, 2H), 7.48 (s, 1H), 5.37 (s, 2H), 4.14 (t, J = 6 Hz, 2H), 3.94 (s, 3H), 1.83 (quint, J = 6 Hz, 2H), 1.35 (quint, J = 6 Hz, 2H), 0.93 (t, J = 6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 165.5, 138.6, 138.3, 137.5, 131.9, 131.3, 124.7, 120.4 (q, $J^{C,F}$ = 315 Hz, NTf_2), 102.2, 54.3, 50.4, 34.5, 32.0, 19.6, 13.4.

3-Butyl-4(5)-(4-iodobenzoyloxymethyl)-1-methyl-3*H*-imidazol-1-ium Toluene-4-sulfonate (5). To a vial containing 0.2590 g of dried ionic liquid **1** (X − OTs) (0.5589 mmol) was added 671 μL of dichloromethane followed by 117 μL (0.8383 mmol) of triethylamine. The resultant mixture was cooled to −20 °C, followed by the dropwise addition of a solution of 45 μL (0.5589 mmol) of 4-iodobenzoyl chloride in 112 μL of dichloromethane. The reaction mixture was left to stir for 30 min and was then quenched using 5 N NaOH (200 μL) followed by dilution with dichloromethane (5 mL) and water (2 mL). The aqueous layer was extracted with dichloromethane (3 × 5 mL). The combined organic extracts were dried (Na_2CO_3) and concentrated in vacuo to afford 0.2892 g (quantitative) of **5** as an off-white solid (mp 164−166 °C): IR ($CHCl_3$) ν_{max} cm^{-1} 3013.0, 2962.5, 2876.5, 1728.3, 1586.0, 1540.2, 1521.3, 1475.8, 1423.1, 1394.7, 1263.0, 1224.8, 1122.5, 1093.6, 1009.4, 928.5, 846.1, 734.1, 671.0, 626.5; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 9.95 (s, 1H), 7.77 (d, J = 11 Hz, 2H), 7.70 (d, J = 11 Hz, 2H), 7.63 (d, J = 7 Hz, 2H), 7.62 (s, 1H), 7.07 (d, 7 Hz, 2H), 5.31 (s, 2H), 4.11 (t, J = 6 Hz, 2H), 3.97 (s, 3H), 2.27 (s, 6H), 1.74 (quint, J = 6 Hz, 2H), 1.27 (quint, J = 6 Hz, 2H), 0.84 (t, J = 6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 165.4, 143.4, 139.8, 138.1, 131.2, 129.7, 128.9, 128.3, 126.0, 122.8, 102.0, 54.6, 49.9, 34.4, 32.0, 21.4, 19.6, 13.5.

3-Butyl-4(5)-(4-diacetoxyiodobenzoyloxymethyl)-1-methyl-3*H*-imidazol-1-ium Triflimide (2). Acetic anhydride and hydrogen peroxide solution (35%) were mixed in a 4:1 ratio at 0 °C and stirred for 6 h. During this time, the solution was allowed to slowly warm to room temperature. The resulting peracetic acid solution was added to a flask containing 0.7659 g (1.1291 mmol) of the RTIL-supported 4-iodobenzoate salt **4** (about 10 mL per 0.66 mmol) at exactly 40 °C and stirred at this temperature for 8 h. The reaction mixture was concentrated in vacuo to remove all of the volatiles. The residual thick colorless oily product **2** (0.8783 g) was used in the following experiments as such without further purification: IR ($CHCl_3$) ν_{max} cm^{-1} 3479.5, 3016.8, 2736.5, 2583.3, 2399.8, 1781.8, 1635.5, 1586.8, 1521.9, 1475.8, 1424.2, 1349.9, 1331.1, 1180.9, 1057.5, 1009.3, 928.6, 849.3, 778.9, 673.0, 625.8; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 8.80 (s, 1H), 8.16 (d, J = 11 Hz, 2H), 8.10 (d, J = 11 Hz, 2H), 7.48 (s, 1H), 5.43 (s, 2H), 4.16 (t, J = 6 Hz, 2H), 3.99 (s, 3H), 1.99 (s, 6H), 1.83 (quint, J = 6 Hz, 2H), 1.35 (quint, J = 6 Hz, 2H), 0.95 (t, J = 6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 179.7, 161.0 (q, J = 41 Hz), 138.5, 137.2, 135.5, 133.8, 131.9, 131.2, 114.4 (q, $J^{C,F}$ = 315 Hz, NTf_2), 54.7, 50.4, 34.5, 31.9, 20.8, 19.5, 16.8, 13.2.

3-Butyl-4(5)-(4-diacetoxyiodobenzoyloxymethyl)-1-methyl-3*H*-imidazol-1-ium 4-methylbenzenesulfonate (6). Acetic anhydride and hydrogen peroxide solution (35%) were mixed in a 4:1 ratio at 0 °C and stirred for 6 h. During this time, the solution was allowed to slowly warm to room temperature. The resulting peracetic acid solution was added to a flask containing 0.7659 g (1.1291 mmol) of the RTIL-supported 4-iodobenzoate salt **5** (about 10 mL per 0.66 mmol) at exactly 40 °C and stirred at this temperature for 8 h. The reaction mixture was concentrated in vacuo to remove all of the volatiles. The residual thick colorless oily product **6** (0.8783 g) was used in the following experiments as such without further purification: IR ($CHCl_3$) ν_{max} cm^{-1} 3384.1, 3010.2, 2681.4, 2585.2, 2436.8, 2400.5, 2336.5, 2255.7, 2218.1, 2068.5, 1778.2, 1692.0, 1586.0, 1521.5, 1477.1, 1423.6, 1231.8, 1121.3, 1086.1, 1030.1, 972.4, 928.4, 888.7, 849.7, 727.8, 671.0, 627.3; ^{1}H NMR (acetone-d_6, 360 MHz) δ (C2 not observed due to facile deuterium exchange in this sample), 8.25 (d, 7 Hz, 2H), 8.17 (d, H = 7 Hz, 2H), 7.98 (s, 1H), 7.68 (d, J = 7 Hz, 2H), 7.15 (d, J = 7 Hz, 2H), 5.60 (s, 2H), 4.31 (t, J = 6 Hz, 2H), 4.12 (s, 3H), 2.30 (s, 3H), 2.09 (s, 6H), 1.85 (obs quint, 2H), 1.35 (quint, J = 6 Hz, 2H), 0.91 (t, J = 6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 179.8, 160.8 (q, J = 43.2 Hz), 143.2, 138.6, 135.6, 133.3, 131.2, 130.2, 129.7, 126.01 123.2, 119.9 (q, NTf_2), 103.0, 55.0, 54.7, 50.4, 34.6, 31.9, 21.5, 20.8, 19.5, 13.2.

3-Butyl-4(5)-(4-hydroxy(tosyloxy)iodobenzoyloxymethyl)-1-methyl-3*H*-imidazol-1-ium Triflimide (3). 4-(Diacetoxyiodo)benzoate derivative **2** (0.3380 g, 0.4243 mmol) was dissolved in 500 μL of acetonitrile. To this solution was added 0.0807 g (0.42430 mmol) of *p*-toluenesulfonic acid monohydrate in 1 mL of acetonitrile. After the mixture was stirred for 1 h, the solvent was removed in vacuo to afford 0.3847 g (100%) of **3** as a pale yellow, viscous liquid. No further purification was attempted and this was used in the tosyloxylation reactions as obtained: IR

($CHCl_3$) ν_{max} cm^{-1} 3472.0, 3017.7, 2584.9, 2400.0, 1776.7, 1599.9, 1522.0, 1462.8, 1424.3, 1349.8, 1331.2, 1156.0, 1057.0, 1034.8, 1009.2, 928.5, 894.6, 849.6, 793.9, 625.9; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 8.63 (s, 1H), 8.32 (d, J = 7 Hz, 2H), 8.21 (d, J = 7 Hz, 2H), 7.70 (d, J = 10 Hz, 2H), 7.50 (s, 1H), 7.28 (d, J = 10 Hz, 2H), 5.49 (s, 2H), 4.15 (t, J = 7 Hz, 2H), 4.01 (s, 3H), 2.20 (s, 3H), 1.85 (quint, J = 6 Hz, 2H), 1.35 (quint, J = 6 Hz, 2H), 0.95 (t, J = 6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 170.7, 161.6 (q, 43.2 Hz), 145.3, 138.6, 137.2, 135.7, 133.9, 132.0, 130.2, 126.7, 123.7, 114.4 (q, $J^{C,F}$ = 315 Hz, NTf_2), 55.3, 50.7, 34.5, 31.9, 21.5, 19.5, 13.0.

3-Butyl-4(5)-(4-hydroxy(tosyloxy)iodobenzoyloxymethyl)-1-methyl-3*H*-imidazol-1-ium 4-methylbenzenesulfonate (7). 4-(Diacetoxyiodo)benzoate derivative **6** (0.2774 g, 0.4028 mmol) was dissolved in 500 μL of acetonitrile. To this solution was added 77 mg (0.4028 mmol) of *p*-toluenesulfonic acid monohydrate in 1 mL of acetonitrile. After the mixture was stirred for 1 h, the solvent was removed in vacuo to afford 0.290 g (95%) of **7** as a pale yellow, viscous liquid. No further purification was attempted, and this was used in the tosyloxylation reactions as obtained: IR ($CHCl_3$) ν_{max} cm^{-1} 3473.1, 3013.8, 2578.9, 2400.0, 1981.3, 1793.1, 1599.6, 1588.3, 1521.9, 1462.2, 1424.5, 1313.8, 1228.9, 1058.7, 1034.8, 1009.0, 928.2, 895.4, 849.3, 733.1, 626.1; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 8.75 (s, 1H), 8.0−7.3 (m, 13H), 5.40 (s, 2H), 4.16 (t, J = 6 Hz, 2H), 3.98 (s, 3H), 2.66 (s, 6H), 1.85 (quint, J = 6 Hz, 2H), 1.35 (quint, J = 6 Hz, 2H), 0.94 (t, J = 6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 166.9, 160.3 (q, J = 43.2 Hz), 144.4, 138.4, 137.41, 135.9, 131.2, 130.2, 130.1, 129.9, 127.7, 126.7, 126.6, 123.1, 119.32, 102.8, 54.8, 50.4, 34.6, 31.9, 21.6, 19.5, 13.2.

General Procedure for the Tosyloxylation Reaction. To a chilled solution of 0.3390 g (0.3912 mmol) of supported Koser's salt **3** in a dry round-bottom flask under argon was added 660 μL (0.6373 mmol) of cyclohexanone and 3.5 mL of acetonitrile. The reaction mixture was then stirred for 2 h at 0 °C, during which time the cloudy reaction mixture became a clear pale yellow solution. The reaction was quenched by the addition of 20 mL of water followed by extraction with dichloromethane (3 × 15 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo to yield the crude product mixture. Purification on silica gel using ethyl acetate/hexanes (20: 80) as eluent yielded 80 mg (76%) of 2-tosyloxycyclohexanone. Further elution with acetonitrile afforded 200 mg (75%) of recovered salt **4**.

Procedure for Tosyloxylation Using Sonication. To 0.9232 g (1.0654 mmol) of supported Koser's salt **3** in a dry round-bottom flask under argon was added 1.0 mL (13.6157 mmol) of acetone and 5.0 mL of acetonitrile. The flask was then lowered into an ultrasound cleaning bath filled with warm (55 °C) water to a depth of 2 in.. The reaction mixture was sonicated for 20 min, during which time the cloudy reaction mixture cleared into a yellowish-brown solution. The reaction was quenched by the addition of 20 mL of water followed by extraction with dichloromethane (3 × 15 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo to afford the crude product which was purified on silica gel using ethyl acetate/hexanes (20:80) as eluent to afford 164 mg (67%) of 2-tosyloxyacetone. Further elution with acetonitrile afford 288.3 mg (40%) of recovered salt **4**.

1-Tosyloxyacetone (toluene-4-sulfonic acid 2-oxopropyl ester): ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.77 (d, J = 6 Hz, 2H), 7.34 (d, J = 6 Hz, 2H), 4.47 (s, 2H), 2.42 (s, 3H), 2.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ201.2, 145.7, 132.4, 130.2, 128.2, 72.2, 26.7, 21.8.

2-Tosyloxycyclopentanone (toluene-4-sulfonic acid 2-oxocyclopentyl ester): ^{1}H NMR ($CDCl_3$) 360 MHz δ 7.84 (d, J = 6 Hz, 2H), 7.35 (d, J = 6 Hz, 2H), 4.71 (dd, J = 6 Hz, 10 Hz, 1H), 2.42 (s, 3H), 2.44−1.92 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 209.6, 145.2, 133.5, 130.0, 128.2, 80.4, 34.5, 29.6, 21.8, 17.0.

2-Tosyloxycyclohexanone (toluene-4-sulfonic acid 2-oxocyclohexyl ester): ^{1}H NMR ($CDCl_3$) 360 MHz δ 7.83 (d, 2H), 7.33 (d, 2H), 4.91−4.87 (m, 1H), 2.55−2.27 (m, 3H), 2.43 (s, 3H), 1.99−1.68 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 202.9, 145.1, 133.4, 129.9, 128.1, 82.0, 40.7, 34.8, 27.1, 23.3, 21.8.

Tosyloxyacetophenone (toluene-4-sulfonic acid 2-oxo-2-phenylethyl ester): ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.84−7.80 (m, 4H), 7.59 (t, J = 6 Hz, 1H), 7.44 (t, J = 6 Hz, 2H), 7.31 (d, J = 6 Hz, 2H), 5.26 (s, 2H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 190.4, 145.4, 134.3, 133.8, 132.6, 130.0, 129.0, 128.2, 128.0, 70.12, 21.8.

2-Tosyloxy-3-pentanone (toluene-4-sulfonic acid 1-methyl-2-oxobutyl ester): ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.84 (d, J = 6 Hz, 2H), 7.35 (d, J = 6 Hz, 2H), 4.71 (q, J = 6 Hz, 1H), 2.60 (q, 6 Hz, 2H), 2.45 (s, 3H), 1.34 (d, J − 6 Hz, 3H), 1.01 (t, J = 6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 209.6, 145.2, 133.5, 130.0, 128.2, 80.4, 34.5, 29.6, 21.8, 17.04.

General Procedure Using Tosylate Salt. To a chilled solution of 0.2996 g (0.3949 mmol) of the tosylate salt **7** in a dry round-bottom flask under argon was added 660 μL (0.6373 mmol) of cyclohexanone and 3.5 mL of acetonitrile. The reaction mixture was then stirred for 6 h at 0 °C, during which time the cloudy reaction mixture became a clear pale yellow solution. The reaction mixture was then diluted with ether (50 mL) precipitating the insoluble RTIL-4-iodobenzoate salt **5**. Vacuum filtration and further washing with ether afforded the recovery of 248 mg (100%) of this salt. The ether washes were then washed with saturated aqueous $NaHCO_3$ (20 mL) and water (20 mL) to removed residual toluenesulfonic acid. The organic layer was then dried with Na_2SO_4, filtered, and concentrated in vacuo. The residual crude was triturated with cold hexanes to afford 83 mg (79%) of 2-tosyloxycyclohexanone.

Acknowledgment. We thank the New York State Energy Research Development Agency (NYSERDA) and the Research Foundation for support of this research.

Supporting Information Available: Spectra for salts **2**−**7** and the α-tosyloxyketone products. This material is available free of charge via the Internet at http://pubs.acs.org.

JO047807K